

EP 42968 3



(19)

Europäisches Patentamt

European Patent Office

Office européen des brevets



(11)

EP 1 207 214 A2

(12)

EUROPEAN PATENT APPLICATION

(43) Date of publication:
22.05.2002 Bulletin 2002/21

(51) Int Cl.7: C22C 38/44, C22C 38/48

(21) Application number: 01126784.6

(22) Date of filing: 09.11.2001

(84) Designated Contracting States:

AT BE CH CY DE DK ES FI FR GB GR IE IT LI LU
MC NL PT SE TR

Designated Extension States:

AL LT LV MK RO SI

(30) Priority: 15.11.2000 JP 2000348068

(71) Applicant: Kawasaki Steel Corporation
Kobe-shi, Hyogo 651-0075 (JP)

(72) Inventors:

• Miyazaki, Atsushi,
Technical Research Laboratories
Chiba-shi, Chiba 260-0835 (JP)

• Hirasawa, Junichiro, Technical Research Labs.
Chiba-shi, Chiba 260-0835 (JP)

• Muraki, Mineo, Technical Research Laboratories
Chiba-shi, Chiba 260-0835 (JP)

• Yazawa, Yoshihiro,
Technical Research Laboratories
Chiba-shi, Chiba 260-0835 (JP)

(74) Representative: Henkel, Feiler, Hänel
Möhlstrasse 37
81675 München (DE)

(54) Soft Cr-containing steel

(57) The soft Cr-containing steel includes, on a % by mass basis, C: from about 0.001% to about 0.020%, Si: more than about 0.10% and less than about 0.50%, Mn: less than about 2.00%, P: less than about 0.060%, S: less than about 0.008%, Cr: from about 12.0% to about 16.0%, Ni: from about 0.05% to about 1.00%, N: less than about 0.020%, Nb: from about $10 \times (C + N)$ to about 1.00%, Mo: more than about 0.80% and less

than about 3.00%, wherein the contents of alloying elements, represented by Si and Mo, respectively, on a % by mass, satisfy the formula $Si \leq 1.2 - 0.4Mo$, so as to prevent precipitation of the Laves phase and to stably secure an effect of increasing high-temperature strength due to solid solution Mo.

EP 1 207 214 A2

Description**BACKGROUND OF THE INVENTION**5 **1. Field of the Invention**

[0001] The present invention relates to a Cr-containing steel. In particular, the present invention relates to a soft Cr-containing steel which has both heat resistance and formability and is suitable for members used in high-temperature environments, for example and especially, exhaust pipes of automobiles and motorcycles, outer casings for catalysts, 10 and exhaust ducts in thermal power plants.

2. Description of the Related Art

[0002] Exhaust system members such as exhaust manifolds, exhaust pipes, converter cases, and mufflers, used in 15 exhaust environments of automobiles are required to have superior formability and superior heat resistance. Conventionally in many cases, Cr-containing steel sheets containing Nb and Si, for example, Type 429 (14Cr-0.9Si-0.4Nb-base) steel, which is malleable, and has superior formability at room temperature, and has relatively increased high-temperature strength, have been used for the aforementioned applications. However, when exhaust gas temperatures 20 are increased to about 900°C, which is higher than can be endured due to improvements of engine performance, there is a problem in that Type 429 steel has an insufficient high-temperature proof stress.

[0003] In order to solve the aforementioned problems, SUS 444 (JIS (Japanese Industrial Standard) G4305, 19Cr-0.2Nb-1.8Mo) steel, which is a Cr-containing steel having improved high-temperature proof stress by addition of Nb and Mo, has been developed. However, there were problems in that the SUS 444 steel was expensive to produce because of the large amounts of alloying elements required, and in particular, molds were significantly worn during 25 use due to high yield strength YS. Furthermore, although a technique related to a stainless steel having superior intergranular corrosion resistance, superior formability into pipes, and superior high-temperature strength has also been disclosed in Japanese Unexamined Patent Application Publication No. 4-228547, since malleability at room temperature was not taken into consideration, there has been a problem in that molds were significantly worn during use.

[0004] Accordingly, requirements for a material having strength equivalent to, or less than, that of Type 429 steel 30 and malleability with excellent workability at room temperature, and having superior high-temperature strength, in order to have a proof stress higher than that of Type 429 steel at 900°C, have become even more intensified. When the high-temperature strength of the material for the exhaust system members is increased, it becomes possible to reduce the thicknesses of the members so as to contribute to reduced weight of automobile bodies. As a consequence, requirements for an increase in high-temperature strength have become even more intensified. Furthermore, accompanying 35 the increase in exhaust gas temperatures, a material for exhaust system members has also been required to have superior oxidation resistance in order to prevent the occurrence of undesired oxidation at high temperatures.

[0005] For example, in Japanese Unexamined Patent Application Publication No. 2000-73147, a Cr-containing steel 40 having superior high-temperature strength, workability, and surface properties has been disclosed as a raw material which can be applied to a wide range of temperatures from the high temperature portion to the low temperature portion of the exhaust system member. This raw material is a Cr-containing steel containing C: 0.02% or less, Si: 0.01% or less, Cr: 3.0% to 20%, and Nb: 0.2% to 1.0%, and precipitation of the Fe₂Nb Laves phase is prevented in order to prevent an increase in yield strength at room temperature, and to impart superior high-temperature strength and workability, as well as excellent surface properties.

[0006] However, there was a problem in that the steel described in Japanese Unexamined Patent Application Publication 45 No. 2000-73147 could not sufficiently satisfy the properties recently required of the material for exhaust system members, since, for example, undesirable oxidation occurred when the steel was heated to a high temperature in the region of 900°C.

SUMMARY OF THE INVENTION

[0007] The present invention was made to solve the aforementioned problems in the conventional techniques and 50 to provide advantages. Accordingly, it is an object of the present invention to provide a soft Cr-containing steel having malleability and superior workability at room temperature, and having, especially, superior high-temperature strength compared to those of conventional steels, as well as superior oxidation resistance. Herein, "malleable at room temperature" means that when the steel is produced under the same conditions as the conventional steels, such as type 429, a strength equivalent to, or less than, those of the conventional steels can be achieved, "superior high-temperature strength" means that a proof stress (0.2% PS) at 900°C is 17 MPa or more, and "superior oxidation resistance" means that undesired oxidation does not occur at 900°C.

[0008] In order to achieve the aforementioned objects, the inventors of the present invention earnestly researched regarding a composition that can significantly improve high-temperature strength without an increase in room-temperature strength of a Cr-containing steel containing Nb. As a result, the inventors of the present invention discovered that regarding the composition, when the Si content was limited to within an appropriate minimum range, the Mo content was appropriately specified in connection with the Si content, and the Cr content was reduced as much as possible, precipitation of the $(\text{Fe,Cr})_2(\text{Mo,Nb})$ Laves phase was prevented and Mo was present primarily in the form of solid solution Mo, and therefore, the Cr-containing steel had malleability at room temperature, and had a significantly improved strength at high temperatures, and the occurrence of undesired oxidation could be prevented.

[0009] That is, according to the present invention, a soft Cr-containing steel having a composition composed of, on a % by mass basis, C: from about 0.001% to about 0.020%, Si: more than about 0.10% and less than about 0.50%, Mn: less than about 2.00%, P: less than about 0.060%, S: less than about 0.008%, Cr: from about 12.0% to about 16.0%, Ni: from about 0.05% to about 1.00%, N: less than about 0.020%, Nb: from about $10 \times (\text{C} + \text{N})$ to about 1.00%, Mo: more than about 0.80% and less than about 3.00%, and Fe and incidental impurities, wherein the contents of alloying elements, silicon and molybdenum, represented by Si and Mo, respectively, on a % by mass basis, satisfy the following formula (1), could be achieved.

$$\text{Si} \leq 1.2 - 0.4\text{Mo}. \quad (1)$$

[0010] In the present invention, the aforementioned soft Cr-containing steel preferably further contains, on a % by mass basis, at least one selected from the group consisting of Cu:

from about 0.05% to about 1.00%, Ti: from about 0.02% to about 0.50%, V: from about 0.05% to about 0.50%, and B: from about 0.0005% to about 0.0100%. The aforementioned soft Cr-containing steels preferably further contain W: from about 0.50% to about 5.00% by mass. The aforementioned soft Cr-containing steels preferably further contain Al: from about 0.02% to about 0.50% by mass. The aforementioned soft Cr-containing steels preferably further contain, on a % by mass basis, at least one selected from the group consisting of REM: from about 0.03% to about 0.10% and Zr: from about 0.05% to about 0.50%.

[0011] In the present invention, regarding the state of Mo in the steel, a ratio of (112) diffraction intensity of the Laves phase, $(\text{Fe,Cr})_2(\text{Mo,Nb})$, to (111) diffraction intensity of Nb carbonitride, $\text{Nb}(\text{C},\text{N})$, A value = $I\{(\text{Fe,Cr})_2(\text{Mo,Nb})\}_{(112)} / I\{\text{Nb}(\text{C},\text{N})\}_{(111)}$, is preferably less than 0.4 based on X-ray diffraction of extraction residues of precipitates in the steel.

BRIEF DESCRIPTION OF THE DRAWINGS

[0012]

Fig. 1 is a graph showing the relationship between the yield strength YS at room temperature and the Si content. Fig. 2 is a graph showing the relationship between the 0.2% proof stress ($\sigma_{0.2\text{at}900^\circ\text{C}}$) at 900°C and the Mo content. Fig. 3 is a graph showing the relationship between the Si content and the Mo content with respect to precipitation of the $(\text{Fe,Cr})_2(\text{Mo,Nb})$ Laves phase.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

[0013] The results of the basic experiments carried out by the inventors of the present invention will now be described.

[0014] Regarding cold rolled Cr-containing steel sheets (sheet thickness: 2 mm) having a base composition of 0.01 mass% C, 0.01 mass% N, 0.3 mass% Mn, 14 mass% Cr, 0.6 mass% Nb, and containing Si and Mo at various contents, the yield strength YS at room temperature and the 0.2% proof stress ($\sigma_{0.2\text{at}900^\circ\text{C}}$) at 900°C were measured. Fig. 1 is a graph showing the relationship between the yield strength YS and the Si content at room temperature with respect to 1.9 mass% Mo-base. In the graph, the ratio of (112) diffraction intensity of the Laves phase, $(\text{Fe,Cr})_2(\text{Mo,Nb})$, to (111) the diffraction intensity of the Nb carbonitride, $\text{Nb}(\text{C},\text{N})$, A value = $I\{(\text{Fe,Cr})_2(\text{Mo,Nb})\}_{(112)} / I\{\text{Nb}(\text{C},\text{N})\}_{(111)}$, based on the X-ray diffraction of the extraction residues of precipitates in the steel, is added to each point with a number in parentheses. The methods for measuring the yield strength YS at room temperature, the 0.2% proof stress ($\sigma_{0.2\text{at}900^\circ\text{C}}$) at 900°C, and the intensity of X-ray diffraction were similar to those in Example 1 as described below. As is shown in Fig. 1, when the Si content exceeds 0.50% by mass, the YS increases significantly. This is believed to be because when the Si content exceeds 0.50% by mass, as is clear from the increase in A value (number in parentheses in Fig. 1), precipitation of the $(\text{Fe,Cr})_2(\text{Mo,Nb})$ Laves phase increases significantly as a result of the increase in the YS. However, the precipitates immediately become coarse with an increase in temperature and, therefore, do not contribute to

the high-temperature strength.

[0015] Fig. 2 is a graph showing the relationship between the 0.2% proof stress ($\sigma_{0.2\text{at}900^\circ\text{C}}$) and the Mo content with respect to each of the bases containing Si with contents of 0.10%, 0.50%, and 0.80% by mass. As is shown in Fig. 2, when the Si content is as high as 0.80% by mass, and large amounts of Laves phase have precipitated, the high-temperature strength barely increases with an increase in the Mo content. On the other hand, it is clear that when the Si content is as low as 0.10% by mass or 0.50% by mass, and precipitation of Laves phase has been prevented, the high-temperature strength tends to increase with an increase in the Mo content. That is, it was discovered that in order to increase the high-temperature strength, it was important to prevent precipitation of Mo as the $(\text{Fe,Cr})_2(\text{Mo},\text{Nb})$ Laves phase (precipitates), and to prevent reduction of the amount of solid solution Mo; and at high temperatures, the solid solution of Mo having a greater atomic radius more effectively contributed to increased high-temperature strength than the $(\text{Fe,Cr})_2(\text{Mo},\text{Nb})$ Laves phase.

[0016] Next, the inventors of the present invention conducted research regarding the relationship between the Mo content and the Si content with respect to precipitation of the $(\text{Fe,Cr})_2(\text{Mo},\text{Nb})$ Laves phase in a Cr-containing steel containing Nb.

[0017] Fig. 3 is a graph showing the relationship between the Si content and the Mo content with respect to precipitation of the $(\text{Fe,Cr})_2(\text{Mo},\text{Nb})$ Laves phase. Herein, points where A values are less than 0.4 are indicated by \circ , and points where A values are 0.4 or more are indicated by \bullet .

[0018] It is clear that precipitation of the Laves phase is prevented and Mo is present as solid solution Mo in the region where the following formula (1) is satisfied:

$$\text{Si} \leq 1.2 - 0.4\text{Mo} \quad (1)$$

(wherein Si and Mo represent the content of respective alloying elements (mass%).)

[0019] The inventors of the present invention also discovered that the $(\text{Fe,Cr})_2(\text{Mo},\text{Nb})$ Laves phase is more likely to precipitate with an increase in the Cr content.

[0020] As described above, it was discovered that in order to significantly increase the high-temperature strength without an increase in the room-temperature strength of a Cr-containing steel containing Nb, it was important to increase the amount of solid solution Mo by adjusting the composition so as to limit the Si content to within an appropriate minimum range, to appropriately specify the Mo content in connection with the Si content, and to reduce the Cr content as much as possible.

[0021] The present invention has been completed with additional research based on the aforementioned findings.

[0022] The reasons for the limitations of the composition of the steel according to the present invention will be described. Herein, mass% is briefly referred to as %.

C: from about 0.001% to about 0.020%

[0023] C is an element for increasing the strength of steel. However, since when the content is 0.020% or more, degradation of the toughness and formability becomes significant, the content was limited to less than 0.020% in consideration of the importance of formability in the present invention. From the viewpoint of the formability, the lower C content is preferred, and the content is desirably 0.008% or less. In order to achieve the desired strength, the content is preferably 0.001% or more, and more preferably 0.002% to 0.008%.

Si: more than about 0.10% and less than about 0.50%

[0024] Si is an element functioning as a deoxidizing agent and improving the oxidation resistance at high temperatures of 900°C or more and, therefore, is one of the most important elements in the present invention. The aforementioned effects are exhibited when the content is more than 0.10%. On the other hand, when the content is 0.5% or more, hardening from use becomes significant, so that the formability is degraded. Therefore, the Si content was limited to more than 0.10%, but less than 0.50%. The content is preferably more than 0.20%, but 0.45% or less.

[0025] Furthermore, Si is an element accelerating the precipitation of the $(\text{Fe,Cr})_2(\text{Mo},\text{Nb})$ Laves phase (Mo Laves phase) so as to increase the room-temperature strength through the precipitation of the Laves phase, and to reduce solid solution Mo with the result that effects of improving high-temperature strength and corrosion resistance due to the solid solution Mo are reduced. Therefore, the Si content must be limited within the range satisfying the relationship between the Si content and the Mo content, $\text{Si} \leq 1.2 - 0.4\text{Mo}$, as described below.

Mn: less than about 2.00%

[0026] Mn functions as a deoxidizing agent. However, when in excess, coarse MnS is formed so as to degrade the formability and the corrosion resistance. Therefore, the Mn content was limited to less than 2.00% in the present invention. The Mn content is preferably 0.60% or less. More preferably, it is 0.20% or less. Further preferably, it is 0.10% or less.

P: less than about 0.060%

[0027] P is an element degrading the toughness, so that it is desirable to reduce the content as much as possible. In addition, from the viewpoint of preventing an increase in P treatment cost, the content was limited to less than 0.060%. The content is preferably 0.03% or less.

S: less than about 0.008%

[0028] S is an element reducing the elongation and the r value and degrading the formability, as well as degrading the corrosion resistance, which is a basic property of stainless steel and, therefore, it is desirable to reduce the content as much as possible. Furthermore, S is an element accelerating precipitation of the Laves phase so as to harden the steel. Therefore, the S content was limited to less than 0.008% in the present invention. Since excessive reduction causes an increase in production cost, the S content is preferably 0.002% or more. More preferably, it is 0.002% to 0.006%.

Cr: from about 12.0% to about 16.0%

[0029] Cr is an element improving the corrosion resistance and oxidation resistance and, therefore, is an important element in the present invention. Furthermore, Cr is an element accelerating the formation of the Laves phase (in the range of the composition of the present invention, $(Fe,Cr)_2(Mo,Nb)$), and when the content is 16.0% or more, precipitation of the Laves phase is accelerated so as to harden the steel. On the other hand, when the content is less than 12.0%, the oxidation resistance and the corrosion resistance are degraded. Accordingly, the Cr content was limited to from about 12.0% to about 16.0%. The Cr content is appropriately chosen within the aforementioned range in accordance with the required levels of oxidation resistance and heat resistance. In particular, in the case where the oxidation resistance is required, the Cr content is preferably from about 14.0% to about 16.0%. More preferably, it is from about 14.0% to about 15.0%.

Ni: from about 0.05% to about 1.00%

[0030] Ni is an element improving the toughness, and in order to exhibit this effect, the Ni content must be 0.05% or more. However, since it is expensive, the Ni content was limited to 1.00% or less. The Ni content is preferably from about 0.05% to about 0.80%. More preferably, it is from about 0.50% to about 0.80%.

N: less than about 0.020%

[0031] N is an element degrading the toughness and the formability of the steel, and when the N content is 0.020% or more, the degradation of the toughness and the formability become significant. Therefore, the N content was limited to less than 0.020%. Preferably, the N content is reduced as much as possible in the present invention, and it is preferably specified to be 0.010% or less.

Nb: from about $10 \times (C + N)$ to about 1.00%

[0032] Nb is an element having such functions as fixing C and N, and improving the high-temperature strength, formability, corrosion resistance, and the intergranular corrosion resistance of welded portions, and these effects are exhibited when the Nb content is $10 \times (C + N)$ or more. On the other hand, when the content is 1.00% or more, large amounts of the Laves phase precipitate so as to increase the room-temperature strength and degrade the toughness and the surface properties. Therefore, the Nb content was limited to from about $10 \times (C + N)$ to about 1.00%. In the case where especially superior high-temperature strength is required, the Nb content is preferably specified to be more than 0.30%. More preferably, it is from about 0.30% to about 0.70%.

Mo: more than about 0.80% and less than about 3.00%

[0033] Mo is as important an element as Si, in the present invention. Since Mo is present in the solid solution state, it has functions such as increasing the high-temperature proof stress and improving the corrosion resistance. These effects are exhibited significantly when the Mo content is more than 0.80%. On the other hand, when the content is 3.00% or more, the Laves phase precipitates significantly with the result that the amount of Mo present in the solid solution state is reduced significantly so as to reduce its contribution to the high-temperature proof stress and corrosion resistance, and the high-temperature strength is increased so as to cause hardening. Accordingly, the Mo content was limited to more than 0.80%, but less than 3.00%. The Mo content is preferably more than 1.50%, but less than 3.00%.

[0034] In the present invention, in order to prevent the precipitation of the Laves phase as much as possible, and to make full use of the solid solution Mo, the content of Mo must be limited within the range satisfying the relationship between the Si content and the Mo content, $Si \leq 1.2 - 0.4Mo$ ($Mo \leq 3 - 2.5Si$), as described below.

[0035] The aforementioned chemical components are contained within the aforementioned range, and Si and Mo are contained so as to satisfy the following formula (1):

$$Si \leq 1.2 - 0.4Mo \quad (1)$$

wherein Si and Mo represent the content of respective alloying elements (mass%). When the formula (1) is not satisfied, as shown in Fig. 3, precipitation of the Laves phase becomes significant. As a consequence, the room-temperature strength is increased so as to cause hardening, and the amount of the solid solution Mo is reduced, so that the effect of improving the high-temperature strength due to the solid solution Mo is reduced.

[0036] In the present invention, the following components can be further contained in addition to the aforementioned components.

[0037] At least one selected from the group consisting of Cu: from about 0.05% to about 1.00%, Ti: from about 0.02% to about 0.50%, V: from about 0.05% to about 0.50%, and B: from about 0.0005% to about 0.0100%

Cu, Ti, V, and B are elements improving the workability and the formability, and at least one of these may be chosen and contained as necessary.

[0038] Cu has a function of improving, especially, the formability and corrosion resistance. Such an effect becomes significant when the content is 0.05% or more. However, when Cu is excessively contained at a content exceeding 1.00%, ϵ -Cu precipitates so as to become brittle. Therefore, the Cu content is preferably limited to 1.00% or less. More preferably, it is from about 0.05% to about 0.10%.

[0039] Ti is an element having a function of improving the formability. Such an effect becomes significant when the content is 0.02% or more. However, when Ti is excessively contained at a content exceeding 0.50%, coarse Ti(C,N) precipitates so as to degrade the surface properties. Therefore, the Ti content is preferably limited to 0.50% or less. More preferably, it is from about 0.02% to about 15(C + N), wherein C represents C content (% by mass) and N represents N content (% by mass).

[0040] V is an element having a function of effectively improving the formability. Such an effect becomes remarkable when the content is 0.05% or more. However, when V is excessively contained at a content exceeding 0.50%, coarse V(C,N) precipitates so as to degrade the surface properties. Therefore, the V content is preferably limited to 0.50% or less. More preferably, it is from about 0.05% to about 20(C + N), wherein C represents C content (% by mass) and N represents N content (% by mass).

[0041] B is an effective element for improving the workability, especially, workability for secondary processing. Such an effect becomes significant when the content is 0.0005% or more. However, when large amounts of B are contained at a content exceeding 0.0100%, BN is generated so as to significantly degrade the workability. Therefore, the B content is preferably limited to 0.0100% or less. More preferably, it is from about 0.0005% to about 0.0050%.

W: from about 0.50% to about 5.00%

[0042] W is an element increasing high-temperature proof stress and improving heat resistance, and may be contained as necessary. Such an effect is exhibited when the content is 0.50% or more. However, when W is excessively contained at a content exceeding 5.00%, the steel is hardened. Therefore, the W content is preferably limited to 5.00% or less. More preferably, it is from about 0.80% to about 3.00%. Further preferably, it is more than 2.00%, but 3.00% or less.

Al: from about 0.02% to about 0.50%

[0043] Al functions as a deoxidizing agent, and may be incidentally contained in the case where Al-deoxidation is

performed, although it may be intentionally contained as necessary. When Al is intentionally contained, it has functions of forming surface protection scale during welding, preventing permeation of C, N, and O from the atmosphere, and improving the toughness of a welded zone. Such an effect is exhibited significantly when the content is 0.02% or more. On the other hand, when the content exceeds 0.50%, the degradation of the workability becomes significant. Therefore, the Al content is preferably limited to 0.50% or less. More preferably, it is more than 0.03%, but 0.20% or less.

[0044] Since REM and Zr improve the oxidation resistance, at least one of them may be chosen and contained as necessary.

REM: from about 0.03% to about 0.10%

[0045] REM (rare-earth element) is an element improving the oxidation resistance, and may be contained as necessary in the present invention. Such an effect is exhibited significantly when the content is 0.03% or more. However, when the content exceeds 0.10%, the steel becomes significantly brittle. Therefore, the REM content is preferably limited to 0.10% or less. More preferably, it is from about 0.03% to about 0.08%.

Zr: from about 0.05% to about 0.50%

[0046] Since Zr improves the oxidation resistance, it may be contained as necessary. This effect is exhibited when the content is 0.05% or more. However, when the content exceeds 0.50%, the steel becomes brittle due to precipitation of Zr intermetallic compounds. Therefore, the Zr content is preferably limited to from about 0.05% to about 0.50%. More preferably, it is from about 0.10% to about 0.40%.

[0047] The state of Mo in the steel: a diffraction intensity ratio based on the X-ray diffraction of the extraction residues of precipitates in the steel, $I\{(Fe,Cr)_2(Mo,Nb)\}_{(112)} / I\{Nb(C,N)\}_{(111)}$, of less than 0.4 is preferable.

[0048] Since the steel according to the present invention contains Nb and Mo, the $(Fe,Cr)_2(Mo,Nb)$ Laves phase is likely to precipitate. When the Laves phase precipitates, the yield strength Y_S is increased significantly at room temperature. However, this Laves phase immediately becomes coarse at a high temperature ($900^{\circ}C$), and does not contribute to the high-temperature strength. Therefore, the $(Fe,Cr)_2(Mo,Nb)$ Laves phase is preferably reduced as much as possible. In the steel according to the present invention, since the Nb content is ten times the C and N content or more, a constant amount of Nb (C,N) precipitates regardless of the amount of Nb. Therefore, it is preferred that the X-ray diffraction intensity from the (112) plane of the $(Fe,Cr)_2(Mo,Nb)$ Laves phase, $I\{(Fe,Cr)_2(Mo,Nb)\}_{(112)}$, relative to the X-ray diffraction intensity from the (111) plane of Nb(C,N), $I\{Nb(C,N)\}_{(111)}$, is reduced, as much as possible, to less than 0.4. Accompanying this, the amount of precipitation of the $(Fe,Cr)_2(Mo,Nb)$ Laves phase is reduced. When this ratio exceeds 0.4, the amount of precipitation of the $(Fe,Cr)_2(Mo,Nb)$ Laves phase is increased, so that the room-temperature strength is increased and the formability is degraded. More preferably, the ratio is less than 0.2.

[0049] The method for producing the steel according to the present invention is not specifically limited, and any general method for producing Cr-containing steel can be used. For example, a molten steel having a predetermined composition within the scope of the present invention is refined by a refining method using a smelting furnace, for example, a converter and an electric furnace, or further using ladle refining, vacuum refining, etc., and then, is made into a slab by a continuous casting method or an ingot-making method. Thereafter, a cold rolled annealed sheet is preferably produced by performing the steps of hot rolling, annealing of the hot-rolled sheet, pickling, cold rolling, final annealing, and pickling in that order. The cold rolling may be performed once, or may be performed two or more times with the intermediate annealing. The steps of cold rolling, final annealing, and pickling may be performed repeatedly. Sometimes, the step of annealing the hot-rolled sheet may be omitted. Furthermore, when luster is required, skin pass, etc., may be performed.

Examples

Example 1

[0050] Fifty kilograms of each steel ingot having a composition shown in Table 1 was prepared. The steel ingot was heated to $1,100^{\circ}C$, and thereafter, was hot-rolled so as to produce a hot rolled sheet having a thickness of 5 mm. The resulting hot rolled sheet was subjected to hot rolled sheet annealing (annealing temperature : $1,000^{\circ}C$), pickling, cold rolling (cold rolling draft: 60%), final annealing (annealing temperature : $1,000^{\circ}C$), and pickling in that order, so that a cold rolled annealed sheet having a thickness of 2 mm was produced.

[0051] Regarding the resulting cold rolled annealed sheet, the high-temperature strength, the formability, and the oxidation resistance were evaluated.

(1) High-temperature strength

[0052] Two tensile test pieces of JIS No. 13B, in which the direction of tensile coincided with the direction of the rolling, were taken from each cold rolled annealed sheet, and a high temperature tensile test was performed in conformity with JIS G 0567 under the conditions of tensile temperature: 900°C and strain rate: 0.3%/min so as to measure the 0.2% proof stress ($\sigma_{0.2at900^{\circ}C}$) at 900°C and an average value of the two test pieces was determined. When $\sigma_{0.2at900^{\circ}C}$ was 17 MPa or more, the high-temperature strength was evaluated to be good (O), and when $\sigma_{0.2at900^{\circ}C}$ was less than 17 MPa, the high-temperature strength was evaluated to be poor (X).

(2) Formability

[0053] Two tensile test pieces of JIS No. 13B were taken from each of three directions of each cold rolled annealed sheet, that is, the direction of the rolling, the direction forming an angle of 45° with the direction of the rolling, and the direction forming an angle of 90° with the direction of the rolling. Then, a room temperature tensile test (test temperature: 20°C) was performed in conformity with JIS Z 2241. Subsequently, an average value of the two test pieces was determined so as to determine the yield strength YS (YS₀, YS₄₅, and YS₉₀). From the resulting yield strength YS of each direction, an average YS was calculated based on the formula, average YS = (YS₀ + 2YS₄₅ + YS₉₀) / 4, and the formability was evaluated based on the resulting average YS. When the average YS was 320 MPa or less, the formability was evaluated to be good (O), and when the average YS exceeded 320 MPa, the formability was evaluated to be poor (X). The reason the formability was evaluated to be good when the average YS was 320 MPa or less is that, as described above, when the conventional steel, Type 429, is produced under the same conditions as those of the steels according to the present invention, the room-temperature strength is 320 MPa. When the steels used in the Examples of the present invention are subjected to skin pass in order to achieve further luster, the room-temperature strength may increase by about 30 MPa. This steel is also included in the scope of the present invention. Regarding Examples of the present invention, in order to compare with the conventional steel, Type 429, under the same production conditions, the formability was evaluated to be good when the room-temperature strength was 320 MPa or less. Although not described in the Examples, steel having a room-temperature strength exceeding 320 MPa due to the addition of a process, for example, skin pass, in accordance with the requirement for luster is also included in the scope of the present invention.

(3) Oxidation resistance

[0054] Two test pieces (2 mm thick × 20 mm wide × 30 mm long) were taken from each cold rolled annealed sheet, and the test pieces were stood at a test temperature of 900°C in air for 400 hours. The weights of the test pieces were measured before and after the test, and the amount of change in weight before and after the test was calculated so as to determine the average value of the two test pieces. From the results thereof, when the amount of the change in weight was within ±5 mg/cm², the oxidation resistance was evaluated to be good (O), and when the amount of the change in weight was more than 5 mg/cm² or less than -5 mg/cm², the oxidation resistance was evaluated to be poor (X).

[0055] The state of Mo present in each cold rolled annealed sheet was estimated based on the X-ray diffraction of the extraction residue. Each cold rolled annealed sheet was electrolyzed in an acetylacetone-based electrolytic solution so as to produce an extraction residue. Regarding the resulting extraction residue, the X-ray diffraction intensity from the (111) plane of Nb(C,N), I{Nb(C,N)}₍₁₁₁₎, and the X-ray diffraction intensity from the (112) plane of the (Fe,Cr)₂(Mo, Nb) Laves phase, I{(Fe,Cr)₂(Mo,Nb)}₍₁₁₂₎, were determined based on the X-ray diffraction, and subsequently, I{(Fe,Cr)₂(Mo,Nb)}₍₁₁₂₎ / I{Nb(C,N)}₍₁₁₁₎ was calculated.

[0056] The results thereof are shown in Table 2.

[0057] Each of the steels of the Examples of the present invention has a yield strength YS of 320 MPa or less at room temperature so as to have low room-temperature strength, and to have malleability equivalent to, or more than, that of Type 429 steel (Steel No. 16) as a conventional example. Furthermore, each of the steels of the Examples of the present invention has a high $\sigma_{0.2at900^{\circ}C}$ of 17 MPa or more so as to have a high-temperature strength superior to those of Type 429 steel (Steel No. 16) and SUS436L steel (JIS G4305, Steel No. 15), as conventional examples. In addition, no undesired oxidations are observed even at 900°C, so that the steels according to the present invention have superior oxidation resistance. On the other hand, the steels of the comparative examples and the conventional examples, which are outside the scope of the present invention, have a yield strength YS exceeding 320 MPa at room temperature so as to have hardness, have a $\sigma_{0.2at900^{\circ}C}$ less than 17 MPa so as to have reduced high-temperature strength, or have degraded oxidation resistance.

[0058] As described above, according to the present invention, a Cr-containing steel suitable for an exhaust system member of an automobile, which exploits the full effect of Mo, has malleability and superior formability at room tem-

EP 1 207 214 A2

perature, has high proof stress and superior heat resistance at high temperatures, and has oxidation resistance at high temperatures, can be produced inexpensively, so that the present invention exhibits significant industrial effects. The steel according to the present invention is also suitable for exhaust path members of thermal-power generation systems which are required to have properties similar to those described above. Furthermore, since the steel according to the present invention contains Mo having an effect of improving corrosion resistance, it can also be applied to uses in which corrosion resistance is required. That is, it can be preferably used for, for example, materials for fuel systems, such as gasoline tanks and fuel supply pipes, materials for mauls, and kitchen appliances, as well as materials for separators of fuel cells and, therefore, the steel according to the present invention has very great industrial significance.

10

15

20

25

30

35

40

45

50

55

5

10

15

20

25

30

35

40

45

50

55

Table 1

Steel No.	C	Si	Mn	P	S	Cr	Ni	Nb	Mo	10 Si<1.2- (C+N) 0.4Mo	Cu	Ti	V	B	W	Al	REM	Remarks	
1	0.005	0.33	0.45	0.028	0.003	14.8	0.15	0.005	0.41	1.71	0.10	0	-	-	-	-	-	-	Example of present invention
2	0.005	0.48	0.08	0.020	0.003	14.9	0.2	0.005	0.40	2.12	0.10	0	-	-	-	-	-	-	Example of present invention
3	0.008	0.25	0.25	0.023	0.002	13.4	0.55	0.009	0.35	1.83	0.17	0	-	-	-	-	-	-	Example of present invention
4	0.005	0.13	0.08	0.018	0.004	12.1	0.25	0.008	0.35	1.63	0.13	0	0.08	-	-	-	-	-	Example of present invention
5	0.009	0.38	0.07	0.019	0.005	14.2	0.65	0.009	0.38	1.31	0.18	0	-	-	-	0.81	-	-	Example of present invention
6	0.004	0.21	0.45	0.033	0.003	15.5	0.61	0.004	0.34	1.81	0.08	0	-	0.08	-	-	-	-	Example of present invention
7	0.012	0.49	0.25	0.022	0.007	14.6	0.91	0.014	0.55	1.92	0.26	0	-	-	0.12	-	-	-	Example of present invention
8	0.011	0.14	0.10	0.031	0.005	14.9	0.25	0.008	0.31	1.61	0.19	0	-	-	-	-	0.02	-	Example of present invention
9	0.009	0.13	0.04	0.024	0.005	14.9	0.61	0.008	0.38	1.71	0.17	0	0.09	-	-	0.0009	-	-	Example of present invention
10	0.008	0.11	0.09	0.018	0.003	14.9	0.35	0.008	0.37	1.61	0.16	0	-	-	0.09	0.0005	-	-	0.05
11	0.009	0.49	0.48	0.018	0.003	15.7	0.24	0.005	0.44	0.92	0.14	0	0.14	-	-	-	-	-	Example of present invention
12	0.008	0.14	0.08	0.023	0.003	14.8	0.45	0.008	0.38	2.11	0.16	0	-	-	-	0.0025	-	0.03	0.06

Steel No.	Chemical component (mass%)												Remarks					
	C	Si	Mn	P	S	Cr	Ni	Nb	Mo	10 (C+N)	Si≤1.2- 0.4Mo	Cu	Ti	V	B	W	Al	REM
13	0.007	0.95	0.03	0.022	0.006	20.4	0.08	0.007	0.54	2.03	0.14	x	-	-	-	-	-	SUS444 Conventional example
14	0.002	0.35	0.11	0.024	0.004	19.5	0.12	0.003	0.55	1.61	0.05	O	0.25	-	-	-	-	SUS444 Conventional example
15	0.008	0.55	0.45	0.033	0.004	18.5	0.22	0.008	-	0.92	0.16	x	-	0.35	-	-	-	SUS436L Conventional example
16	0.004	0.98	0.45	0.028	0.003	14.9	0.15	0.004	0.49	=	0.08	O	-	-	-	-	-	Type429 Conventional example
17	0.008	0.48	0.15	0.033	0.003	15.4	0.22	0.009	0.38	2.01	0.17	x	0.15	-	-	-	-	Comparative example
18	0.012	0.04	0.15	0.020	0.003	14.8	0.25	0.009	0.35	0.92	0.21	O	-	-	-	-	-	Comparative example
19	0.007	0.11	0.25	0.033	0.003	14.9	0.15	0.005	0.44	3.11	0.12	x	-	-	-	-	-	Comparative example
20	0.005	0.33	0.41	0.031	0.010	14.8	0.23	0.007	0.41	1.61	0.12	O	-	-	-	-	-	Comparative example
21	0.005	0.31	0.41	0.031	0.003	14.5	0.31	0.005	1.12	1.72	0.10	O	-	-	-	-	-	Comparative example
22	0.004	0.21	0.41	0.025	0.003	12.6	0.03	0.003	0.31	1.51	0.07	O	-	-	-	2.51	-	Example of present invention
23	0.006	0.15	0.05	0.015	0.004	13.1	0.03	0.004	0.35	1.61	0.10	O	-	-	-	2.11	-	Zr: 0.28 Example of present invention
24	0.004	0.35	0.95	0.021	0.003	14.9	0.25	0.007	0.41	1.55	0.11	O	0.13	-	-	-	-	Example of present invention
25	0.004	0.33	1.78	0.021	0.002	12.7	0.55	0.005	0.49	1.61	0.09	O	-	-	-	2.59	-	Example of present invention

Table 1 (continued)

Table 2

Steel No.	{(Fe,Cr) ₂ (Mo,Nb) ₁₁₂ } {Nb(C,N)} ₁₁₁	Ordinary-temperature strength			High-temperature strength		Oxidation resistance		Remarks
		YS MPa	Evaluation	$\sigma_{0.2}$ at 900 °C	Evaluation	$\sigma_{0.2}$ at 900 °C	Evaluation	$\sigma_{0.2}$ at 900 °C	
1	0.21	300	○	18	○	○	○	○	Example of present invention
2	0.29	320	○	20	○	○	○	○	Example of present invention
3	0.08	290	○	20	○	○	○	○	Example of present invention
4	0.00	280	○	19	○	○	○	○	Example of present invention
5	0.18	300	○	20	○	○	○	○	Example of present invention
6	0.18	290	○	20	○	○	○	○	Example of present invention
7	0.27	310	○	20	○	○	○	○	Example of present invention
8	0.00	290	○	19	○	○	○	○	Example of present invention
9	0.00	290	○	20	○	○	○	○	Example of present invention
10	0.00	280	○	19	○	○	○	○	Example of present invention
11	0.24	310	○	17	○	○	○	○	Example of present invention
12	0.22	310	○	22	○	○	○	○	Example of present invention
13	0.71	390	×	18	○	○	○	○	Conventional example
14	0.61	350	×	18	○	○	○	○	Conventional example
15	0.00	300	○	15	×	○	○	○	Conventional example
16	0.33	320	○	15	×	○	○	○	Conventional example
17	0.51	350	×	18	○	○	○	○	Comparative example
18	0.00	270	○	17	○	×	○	○	Comparative example
19	0.45	390	×	22	○	○	○	○	Comparative example
20	0.45	341	×	18	○	○	○	○	Comparative example
21	0.81	390	×	22	○	○	○	○	Comparative example
22	0.12	320	○	25	○	○	○	○	Example of present invention
23	0.05	310	○	24	○	○	○	○	Example of present invention

Table 2 (continued)

Steel No.	{Nb(C,N)} ₁₁₁	Ordinary-temperature strength		High-temperature strength		Oxidation resistance	Remarks
		YS MPa	Evaluation	$\sigma_{0.2}$ at 900 °C	Evaluation		
24	0.00	305	○	19	○	○	Example of present invention
25	0.35	320	○	25	○	○	Example of present invention

Claims

1. A soft Cr-containing steel having a composition, on a % by mass basis, comprising:

C: from about 0.001% to about 0.020%;
 Si: more than about 0.10% and less than about 0.50%;
 Mn: less than about 2.00%;
 P: less than about 0.060%;
 S: less than about 0.008%;
 Cr: from about 12.0% or more to about 16.0%;
 Ni: from about 0.05% to about 1.00%;
 N: less than about 0.020%;
 Nb: from about $10 \times (C + N)$ to about 1.00%;
 Mo: more than about 0.80% and less than about 3.00%; and
 Fe and incidental impurities,

wherein the contents of alloying elements, silicon and molybdenum, represented by Si and Mo, respectively, on a % by mass basis, satisfy the following formula (1):

$$Si \leq 1.2 - 0.4Mo. \quad (1)$$

2. The soft Cr-containing steel according to Claim 1, wherein the content of Mo is more than about 1.50% and less than about 3.00% by mass in the composition.
3. The soft Cr-containing steel according to Claim 1, further comprising, on a % by mass basis, at least one selected from the group consisting of Cu: from about 0.05% to about 1.00%, Ti: from about 0.02% to about 0.50%, V: from about 0.05% to about 0.50%, and B: from about 0.0005% to about 0.0100%.
4. The soft Cr-containing steel according to Claim 2, further comprising, on a % by mass basis, at least one selected from the group consisting of Cu: from about 0.05% to about 1.00%, Ti: from about 0.02% to about 0.50%, V: from about 0.05% to about 0.50%, and B: from about 0.0005% to about 0.0100%.
5. The soft Cr-containing steel according to Claim 1, further comprising W: from about 0.50% to about 5.00% by mass.
6. The soft Cr-containing steel according to Claim 2, further comprising W: from about 0.50% to about 5.00% by mass.
7. The soft Cr-containing steel according to Claim 3, further comprising W: from about 0.50% to about 5.00% by mass.
8. The soft Cr-containing steel according to Claim 1, further comprising Al: from about 0.02% to about 0.50% by mass.
9. The soft Cr-containing steel according to Claim 2, further comprising Al: from about 0.02% to about 0.50% by mass.
10. The soft Cr-containing steel according to Claim 3, further comprising Al: from about 0.02% to about 0.50% by mass.
11. The soft Cr-containing steel according to Claim 4, further comprising Al: from about 0.02% to about 0.50% by mass.
12. The soft Cr-containing steel according to Claim 1, further comprising, on a % by mass basis, at least one element selected from the group consisting of REM: from about 0.03% to about 0.10% and Zr: from about 0.05% to about 0.50%.
13. The soft Cr-containing steel according to Claim 2, further comprising, on a % by mass basis, at least one element selected from the group consisting of REM: from about 0.03% to about 0.10% and Zr: from about 0.05% to about 0.50%.
14. The soft Cr-containing steel according to Claim 3, further comprising, on a % by mass basis, at least one element selected from the group consisting of REM: from about 0.03% to about 0.10% and Zr: from about 0.05% to about 0.50%.

EP 1 207 214 A2

15. The soft Cr-containing steel according to Claim 4, further comprising, on a % by mass basis, at least one element selected from the group consisting of REM: from about 0.03% to about 0.10% and Zr: from about 0.05% to about 0.50%.

5 16. The soft Cr-containing steel according to Claim 5, further comprising, on a % by mass basis, at least one element selected from the group consisting of REM: from about 0.03% to about 0.10% and Zr: from about 0.05% to about 0.50%.

10 17. The soft Cr-containing steel according to Claim 1,
wherein regarding the state of Mo in the steel, a ratio of (112) diffraction intensity of the Laves phase, $(\text{Fe,Cr})_2(\text{Mo}, \text{Nb})$, to (111) diffraction intensity of Nb carbonitride, $\text{Nb}(\text{C,N})$, A value = $I\{(\text{Fe,Cr})_2(\text{Mo}, \text{Nb})\}_{(112)} / I\{\text{Nb}(\text{C,N})\}_{(111)}$, is less than 0.4 based on X-ray diffraction of extraction residues of precipitates in the steel.

15

20

25

30

35

40

45

50

55

FIG. 1

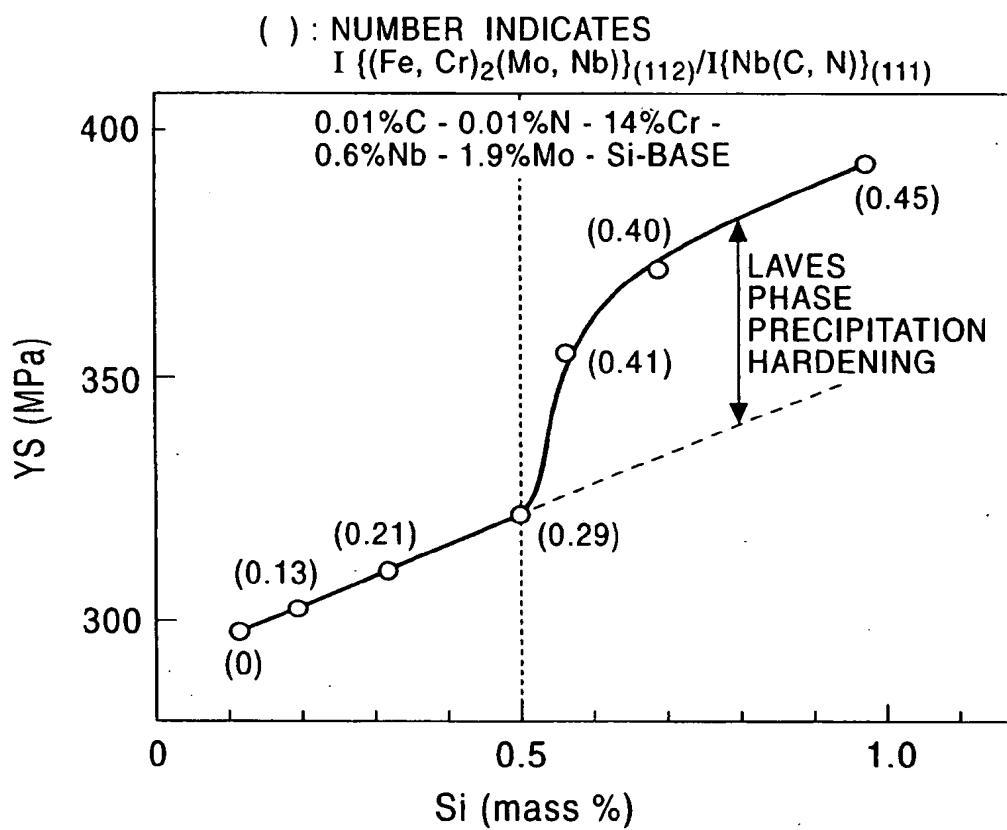


FIG. 2

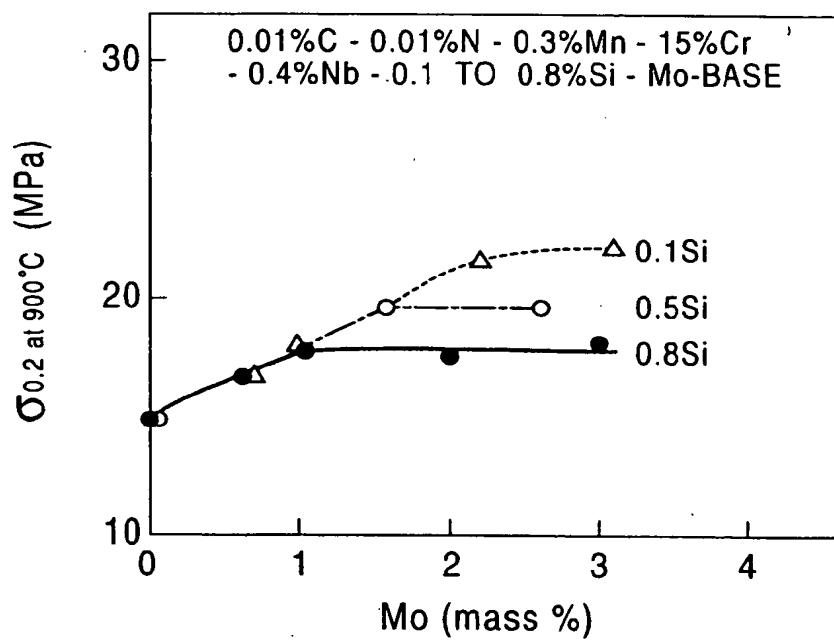
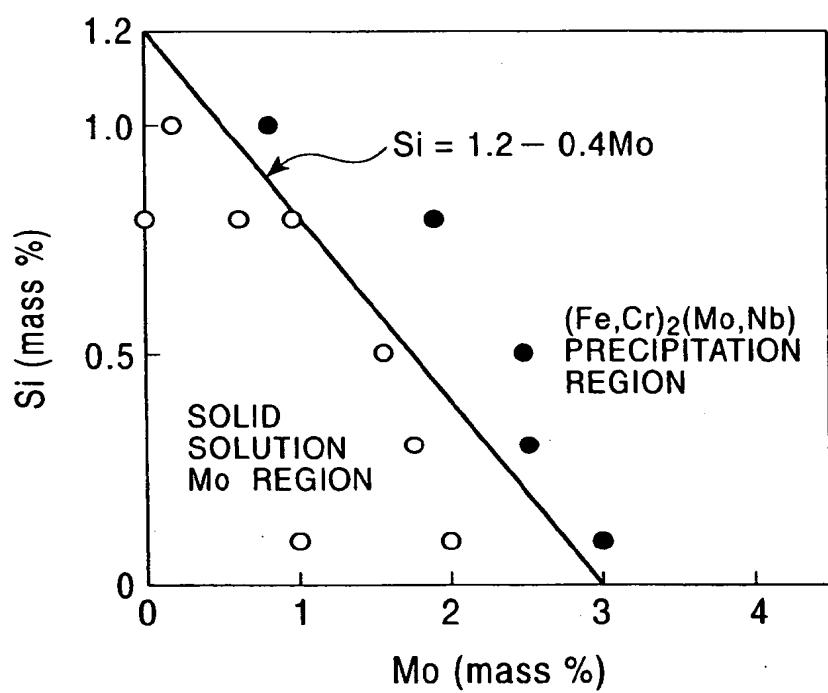


FIG. 3



(19)



Europäisches Patentamt
European Patent Office
Office européen des brevets



(11)

EP 1 207 214 A3

(12)

EUROPEAN PATENT APPLICATION

(88) Date of publication A3:
05.04.2006 Bulletin 2006/14

(51) Int Cl.:
C22C 38/44 (2006.01) **C22C 38/48 (2006.01)**

(43) Date of publication A2:
22.05.2002 Bulletin 2002/21

(21) Application number: 01126784.6

(22) Date of filing: 09.11.2001

(84) Designated Contracting States:
AT BE CH CY DE DK ES FI FR GB GR IE IT LI LU
MC NL PT SE TR

Designated Extension States:
AL LT LV MK RO SI

(30) Priority: 15.11.2000 JP 2000348068

(71) Applicant: JFE Steel Corporation
Tokyo (JP)

(72) Inventors:

- Miyazaki, Atsushi,
Technical Research Laboratories
Chiba-shi,
Chiba 260-0835 (JP)
- Hirasawa, Junichiro,
Technical Research Labs.
Chiba-shi,
Chiba 260-0835 (JP)

- Muraki, Mineo,
Technical Research Laboratories
Chiba-shi,
Chiba 260-0835 (JP)

- Yazawa, Yoshihiro,
Technical Research Laboratories
Chiba-shi,
Chiba 260-0835 (JP)

- Furukimi, Osamu,
Technical Research Laboratories
Chiba-shi,
Chiba 260-0835 (JP)

(74) Representative: Henkel, Feiler & Hänel
Möhlstrasse 37
81675 München (DE)

(54) Soft Cr-containing steel

(57) The soft Cr-containing steel includes, on a % by mass basis, C: from about 0.001% to about 0.020%, Si: more than about 0.10% and less than about 0.50%, Mn: less than about 2.00%, P: less than about 0.060%, S: less than about 0.008%, Cr: from about 12.0% to about 16.0%, Ni: from about 0.05% to about 1.00%, N: less than about 0.020%, Nb: from about $10 \times (C + N)$ to about 1.00%, Mo: more than about 0.80% and less than about

3.00%, wherein the contents of alloying elements, represented by Si and Mo, respectively, on a % by mass, satisfy the formula $Si \leq 1.2 - 0.4Mo$, so as to prevent precipitation of the Laves phase and to stably secure an effect of increasing high-temperature strength due to solid solution Mo.

EP 1 207 214 A3



European Patent
Office

EUROPEAN SEARCH REPORT

Application Number
EP 01 12 6784

DOCUMENTS CONSIDERED TO BE RELEVANT			CLASSIFICATION OF THE APPLICATION (IPC)
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	
X	EP 0 435 003 A (NIPPON STEEL CORPORATION) 3 July 1991 (1991-07-03) * claims 1-3 * * column 1, line 1 - column 3, line 42 * * column 5, line 10 - column 8, line 11 * * table 1 * -----	1-17	C22C38/44 C22C38/48
X	PATENT ABSTRACTS OF JAPAN vol. 1998, no. 14, 31 December 1998 (1998-12-31) -& JP 10 237600 A (SUMITOMO METAL IND LTD), 8 September 1998 (1998-09-08) * abstract *	1-17	
X	EP 0 638 653 A (NIPPON STEEL CORPORATION) 15 February 1995 (1995-02-15)	1-4,	
A	* claims 1,2 *	8-11,17 5-7, 12-16	
	* page 4, line 5 - page 5, line 55 * * table 1 *		
X	PATENT ABSTRACTS OF JAPAN vol. 1996, no. 09, 30 September 1996 (1996-09-30) -& JP 08 120417 A (SUMITOMO METAL IND LTD), 14 May 1996 (1996-05-14)	1-4, 8-11,17	
A	* abstract *	5-7, 12-16	
A	PATENT ABSTRACTS OF JAPAN vol. 1995, no. 06, 31 July 1995 (1995-07-31) -& JP 07 062498 A (MITSUBISHI HEAVY IND LTD), 7 March 1995 (1995-03-07) * abstract *	1-17	
	----- -/-		
The present search report has been drawn up for all claims			
1	Place of search	Date of completion of the search	Examiner
	The Hague	31 January 2006	Vlassi, E
CATEGORY OF CITED DOCUMENTS		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document	
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document			



EUROPEAN SEARCH REPORT

Application Number
EP 01 12 6784

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
D,A	PATENT ABSTRACTS OF JAPAN vol. 2000, no. 06, 22 September 2000 (2000-09-22) -& JP 2000 073147 A (KAWASAKI STEEL CORP), 7 March 2000 (2000-03-07) * abstract * ----- A EP 0 930 375 A (KAWASAKI STEEL CORPORATION; JFE STEEL CORPORATION) 21 July 1999 (1999-07-21) * claims 1-9 * * table 1 * ----- A PATENT ABSTRACTS OF JAPAN vol. 1996, no. 05, 31 May 1996 (1996-05-31) -& JP 08 003698 A (KAWASAKI STEEL CORP), 9 January 1996 (1996-01-09) * abstract * -----	1-17 1-17 1-17	
			TECHNICAL FIELDS SEARCHED (IPC)
1	The present search report has been drawn up for all claims		
	Place of search The Hague	Date of completion of the search 31 January 2006	Examiner Vlassi, E
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document			
T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document			

**ANNEX TO THE EUROPEAN SEARCH REPORT
ON EUROPEAN PATENT APPLICATION NO.**

EP 01 12 6784

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report.
The members are as contained in the European Patent Office EDP file on
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

31-01-2006

Patent document cited in search report		Publication date		Patent family member(s)		Publication date
EP 0435003	A	03-07-1991	DE	69018598 D1		18-05-1995
			DE	69018598 T2		17-08-1995
			US	5110544 A		05-05-1992
JP 10237600	A	08-09-1998	NONE			
EP 0638653	A	15-02-1995	DE	69422557 D1		17-02-2000
			JP	6220545 A		09-08-1994
			WO	9417215 A1		04-08-1994
			KR	139016 B1		15-07-1998
			US	5492575 A		20-02-1996
JP 08120417	A	14-05-1996	NONE			
JP 07062498	A	07-03-1995	NONE			
JP 2000073147	A	07-03-2000	JP	3546714 B2		28-07-2004
EP 0930375	A	21-07-1999	DE	69824384 D1		15-07-2004
			DE	69824384 T2		14-10-2004
			ES	2222598 T3		01-02-2005
			WO	9907909 A1		18-02-1999
			TW	452599 B		01-09-2001
			US	6113710 A		05-09-2000
JP 08003698	A	09-01-1996	JP	3446383 B2		16-09-2003